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(54) Preparation of 1,1,1,3-tetrafluoropropene(1234ze)

Herstellung von 1,1,1,3-Tetrafluorpropen (1234ze)

Préparation du 1,1,1,3-tétrafluoropropène (1234ze)

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Description

[0001] This invention relates to preparation of cis/trans 1,1,1,3-tetrafluoropropene ("1234ze"), a monomer useful for the preparation of various homopolymers and copolymers, particularly to processes for the dehydrofluorination of 1,1,1,3,3-pentafluoropropane ("245fa"), a known blowing agent, to 1234ze using a chromium-based catalyst. While the prior art, R. N. Haszeldine, J. Chem. Soc., 1952 (3490), describes the synthesis of cis/trans 1,1,1,3-tetrafluoropropene by fluorination of 1,1,1-trifluoro-2-propyne, this latter feed stock material is not available commercially. Knunyants et al, in Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences 1960 pages 1312 to 1317, incidentally describe a conversion of 1,1,1,3,3-pentafluoropropane to 1234ze using KOH powder suspended in ether.

[0002] We propose herein a process for the preparation of 1234ze by contacting 245fa with a chromium-based catalyst and recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

[0003] In the prior art, WO96/05157 proposes a Cr₂O₃ catalyst for use in dehydrofluorination reactions, exemplified by the preparation of trifluoroethylene from 1,1,1,2-tetrafluoroethane. Other chromium catalyst disclosures include EP234002, which uses chromium oxyfluoride to convert 1,1,1-trifluoro compounds to 1,1-difluoro compounds, and WO96/41679 and JP-A-54/130507, which use a fluorided Cr₂O₃ catalyst to convert 1,1-difluoroethane to vinyl fluoride and vinylidene fluoride respectively.

[0004] The process of the present invention comprises a process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an oxygen-containing gas in the presence of a fluorided catalyst selected from Cr₂O₃ and Cr/Ni/AlF₃, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

[0005] The catalyzed process is preferably carried out in the gas phase. Use of the oxygen-containing gas such as air is to extend the catalyst lifetime, the level of oxygen generally being from about 1 to about 10 volume percent (preferably about 2 to 5%), based on the volume of the organic feed. Temperatures of from about 100°C. to about 600°C. are typically used, preferably from about 300°C. to about 400°C. The pressure can be atmospheric. Contact time (total flow rate per catalyst volume) is typically from about 1 to about 60 seconds, preferably from about 20 to 50 seconds. The catalyst is a fluorided chromium-based catalyst such as fluorided chromium oxide, Cr₂O₃, which chromium-based catalyst is either unsupported or supported on a support such as activated carbon, graphite, fluorided graphite or fluorided alumina, the chromium catalyst being used alone or in the presence of a co-catalyst selected from

a nickel, cobalt, manganese or zinc salt. Two such preferred chromium catalysts are high surface area chromium oxide and chromium/nickel on fluorided alumina (Cr/Ni/AlF₃), preparation of this latter catalyst being taught, for example, in European Patent 486333. The chromium-based catalysts are preferably activated before use, typically by a procedure wherein the catalyst bed is heated to about 370°-380°C. (normally with a continuous flow of nitrogen), after which a mixture of approximately equal volumes of HF and air or nitrogen (preferably nitrogen) are fed over the catalyst bed for about 18 hours.

[0006] The following examples are illustrative.

[0007] Example 1. 52.4 Grams of a high surface area Cr₂O₃ catalyst was activated by first feeding 30 ccm of nitrogen for 2 hours at 370°C, followed by cofeeding 30 ccm of HF and 30 ccm of nitrogen for 18 hours at 370°C. Subsequently, a mixture of 20 ccm of 245fa and 3 ccm of air (equal to about 3 volume % of oxygen, based on the 245fa volume) was fed over the catalyst bed at 400°C for a contact time of 45 seconds. Conversion was 96.2%. Selectivity for the desired (1234ze) product was about 96.3% (about 18.5% cis, about 77.8% trans). Performance of the catalyst was steady for 360 hours.

[0008] Example 2. Example 1 was repeated using Cr/Ni/AlF₃ catalyst (activated at 370°C. using a cofeed of 30 ccm of nitrogen and 30 ccm of HF for 18 hours) in a series of 3 tests, using the same temperature and air/245fa feed ratio, but with the contact time between 26 and 39 seconds. Conversions ranged from 88 to 94.5%. Selectivity for the desired (1234ze) product ranged from 96.2 to 98.5% (17.7 to 20.5% cis, 77 to 80.5% trans).

Claims

1. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an oxygen-containing gas in the presence of a fluorided catalyst selected from Cr₂O₃ and Cr/Ni/AlF₃, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.
2. A process as in Claim 1 wherein the catalyst is fluorided Cr₂O₃.
3. A process as in Claim 1 wherein the catalyst is fluorided Cr/Ni/AlF₃.
4. A process as in any one of claims 1 to 3 in which the oxygen-containing gas is air.
5. A process as in any of the preceding claims in which the level of oxygen in an organic feed to the catalyst is from 1 to 10 vol% based on the volume of the organic feed.

6. A process as in claim 5 in which said level of oxygen is from 2 to 5 vol%.
7. A process as in any one of the preceding claims in which the temperature is from 300°C to 400°C.
8. A process as in any one of the preceding claims in which the contact time, defined as total rate of flow divided by volume of catalyst, is from 20 to 50s.
9. A process as in any one of the preceding claims in which the fluoridized catalyst is activated before use.

Patentansprüche

1. Verfahren zur Herstellung von cis/trans-1,1,1,3-Tetrafluor-2-propen, umfassend (a) Kontaktierung von 1,1,1,3,3-Pentafluorpropan mit einem Sauerstoffhaltenden Gas in Gegenwart eines fluorierten Katalysators, ausgewählt aus Cr_2O_3 und $\text{Cr}/\text{Ni}/\text{AlF}_3$, und (b) Gewinnung von cis/trans-1,1,1,3-Tetrafluor-2-propen aus dem resultierenden Reaktionsgemisch.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass der Katalysator fluoridiertes Cr_2O_3 ist.
3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass der Katalysator fluoridiertes $\text{Cr}/\text{Ni}/\text{AlF}_3$ ist.
4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass das Sauerstoffhaltende Gas Luft ist.
5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass der Sauerstoffgehalt in der organischen Beschickung für den Katalysator 1 bis 10 Vol.-%, bezogen auf das Volumen der organischen Beschickung, beträgt.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, dass der Sauerstoffgehalt 2 bis 5 Vol.-% beträgt.
7. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Temperatur 300°C bis 400°C beträgt.
8. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Kontaktzeit, definiert als Gesamtrate des Flusses, dividiert durch das Katalysatorvolumen, 20 bis 50 s beträgt.
9. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass der fluori-

derte Katalysator vor dem Gebrauch aktiviert wird.

Revendications

5. Procédé pour la préparation de cis/trans-1,1,1,3-tétratrafluoro-2-propène, qui comprend les étapes consistant (a) à mettre en contact du 1,1,1,3,3-pentafluoropropane avec un gaz contenant de l'oxygène en présence d'un catalyseur fluoré choisi entre Cr_2O_3 et $\text{Cr}/\text{Ni}/\text{AlF}_3$, et (b) à recueillir le cis/trans-1,1,1,3-tétratrafluoro-2-propène à partir du mélange réactionnel résultant.
15. Procédé suivant la revendication 1, dans lequel le catalyseur consiste en Cr_2O_3 fluoré.
20. Procédé suivant la revendication 1, dans lequel le catalyseur consiste en $\text{Cr}/\text{Ni}/\text{AlF}_3$ fluoré.
25. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le gaz contenant de l'oxygène est l'air.
30. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la quantité d'oxygène dans une charge organique d'alimentation amenée au catalyseur est comprise dans l'intervalle de 1 à 10 % en volume sur la base du volume de la charge organique d'alimentation.
35. Procédé suivant la revendication 5, dans lequel la dite quantité d'oxygène est comprise dans l'intervalle de 2 à 5 % en volume.
40. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la température est comprise dans l'intervalle de 300°C à 400°C.
45. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le temps de contact, défini par la vitesse totale d'écoulement divisée par le volume de catalyseur, est compris dans l'intervalle de 20 à 50 s.
50. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le catalyseur fluoré est activé avant utilisation.
- 55.

